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(72) Inventors: IOAN TINCUL
ANDREI GRIGORESCU
DAN VLAHELI

(19)

(54) POLYMERIZATION PROCESS OF ETHYLENE

(71) We, COMBINATUL PETROCHIMIC PITESTI, a Rumanian State Enterprise of Pitesti, Rumania, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the polymerization of ethylene at high pressure in the presence of an organic peroxy compound as polymerization initiator.

In the literature are described many ethylene polymerization processes that lead to the production of a wide range of types of polyethylene with different properties.

Known processes for the polymerization of ethylene at high pressure result in a range of polymers having densities between 0.900 and 0.935 and are based mainly on the use of two types of reactors namely: autoclave and tubular reactors. The autoclave reactor has one or more reaction zones separated by baffles which are attached to a stirrer and exothermic processes are used in which the heat of reaction is taken up by cold ethylene entering the reactor and is removed together with the reaction mixture.

The types of ethylene polymers which are manufactured at a high pressure using the autoclave reactor are used for film, blowing, injection, insulation and they are characterised by the combination of features such as good mechanical strength and chemical resistance, insulating electrical properties and clearness in thin film. For initiating the polymerization process a wide range of organic peroxy compounds are used such as: lauroyl peroxide, diterbutylperoxide, terbutylperacetate, terbutylperoxyisobutyrate, caprylyl peroxide.

The properties of the polymer obtained are mainly affected by pressure, temperature, flow and purity of ethylene. By control of one of the variables: temperature, pressure and ethylene purity or by control of the three variables together, at a constant flow, different properties of the polymer can be ensured.

An increase in flow of ethylene fed into the reactor, for usual types of peroxidic initiators, adversly affects the polyethylene properties. Thus, the increase of ethylene flow leads to an increase in the swelling ratio due to a rise in the degree of chain branching produced because of an increased concentration of free radicals at high reaction rates. Similarly affected are the opacity, clearness and film lustre. For maintaining a steady reaction at the top of the reaction vessel, at a constant rate of conversion, with increase of cold ethylene flow introduced, it is necessary to increase the reaction temperature. This results on the one hand in an adverse affect on the properties and on the other hand in an increase in the consumption of initiators and solvent for the initiators. There are known processes that use initiators which decompose at low temperatures such as: terbutylperpivalate, diisopropylperoxydicarbonate, terbutylperacetate, terbutylperoxyisopropylcarbonate, but they are handled with difficulty, require special storing facilities, and mostly give rise to uncontrollable reaction.

An object of the present invention is to provide a method of polymerizing ethylene at high pressure, for example, in an autoclave reactor, which involves the use of an initiator which has a high activity, which is easy to handle, and which can allow the production at high flow rates and in readily controllable reaction conditions of polymers with improved utilization properties.

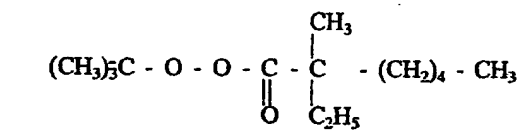
According to the invention therefore there is provided a method for the polymerization of ethylene in one or more reaction zone at a pressure of over 400 atm. and a temperature of 100-300°C in the presence in at least one of the reaction zone of terbutyl

perneodecanoate (as hereinafter defined) which is introduced as a 5-40% by weight solution in isododecane.

According to this invention, polyethylene of low density with good characteristics of utilization in the fields of films, cable, insulation, injection, blowing, can be produced.

The ethylene can be polymerized in two or more reaction zones, with the temperature of each zone being in the range of 100 to 300°C and the pressure of each zone being in the range of 400 to 3000 atm.. The terbutyl perneodecanoate may be introduced only into the first zone and at a temperature substantially lower than the temperature in the other zones.

As used herein, the term terbutyl perneodecanoate is intended to refer to the perester of perneodecanoic acid which has the formula:



It is known that the esterification leads to a specific stabilization of the free radical centre and to a decrease in the dissociation energy. With regard to the tertiary carbon atom, it is known that the effect of steric repulsion usually increases exponentially with the degree of alkylation.

It is assumed that the relaxation of the transition stress from the tetrahedric carbon atom to the crossed triangular centre Sp^2, leads to stronger reactions for voluminous substituents as compared with those that are less voluminous.

Consequently the initiator used, has a low activation energy, high stability of radicals produced and therefore excellent initiation qualities. The initiator is supplied to the reaction vessel in the hydrocarbon solvent in a concentration of 5 - 40% by weight. Due to the excellent solubility it can be used together with a very wide range of solvents at ambient temperature.

As mentioned above, the polymerization process can be effected in two or more zones. in this case the terbutyl perneodecanoate may be introduced into the first zone and the working temperature may be maintained at 130 to 210°C. In the following zone or zones a greater temperature or progressively greater temperatures are created by using terbutyl peroxide, nonanoyl peroxide, terbutyl perbenzoate, lauroyl peroxide, terbutyl peroctoate, terbutyl perisobutyrate, dicumylperoxide, diisobutylperoxide or acetylperoxide.

It is possible to use one or more ethylene inputs and the entire quantity can be introduced into the first zone or gradually along the reactor.

The ethylene feed temperature may be 0-60°C.

The reactor may be provided with a stirrer with paddles or turbines.

The process may be carried out with or without modifying agents or chain transfer agents.

The invention is not intended to be restricted to the production of ethylene homopolymers and can be applied also to ethylene copolymerization with different comonomers.

Examples of polymerization processes will now be described:

Example 1

Ethylene is compressed and supplied to an autoclave reactor with a capacity of 250 l provided with a stirrer and divided into three reaction zones by baffles attached to the stirrer. The zones are fed with different reactants as follows:

Zone 1 - 10.000 kg/h of ethylene, together with 42 l/h of lauroyl peroxide solution in concentration of 30% by weight in white light oil;

Zone II - 2.000 kg/h of ethylene together with 10 l/h of terbutyl perbenzoate solution in concentration of 6% by weight in white light oil;

Zone III - 2.9 l/h of diterbutylperoxide solution in concentration of 3% by weight in white light oil.

Ethylene input temperature = 40°C

Reaction pressure = 1350 atm.

Temperatures for each zone:

Zone I = 185°C

Zone II = 235°C

Zone III = 280°C

With these conditions 2.200 kg/h of polyethylene is produced with properties as shown in Table I.

Example 2

The ethylene is compressed and supplied to a reactor similar to that of Example I. The reactants fed to the reaction zones are as follows:
Zone I - 11,250 kg/h of ethylene together with 50 l/h of lauroyl peroxide solution in concentration of 30% by weight in mineral oil;
Zone II - 3,750 kg/h of ethylene together with 12.5 l/h of terbutylperbenzoate solution in concentration of 6% by weight in mineral oil;
Zone III - 3 l/h of diterbutyl peroxide solution in concentration of 3% by weight in mineral oil.
Ethylene input temperature = 40°C;
Reaction pressure = 1400 atm.
Temperatures for each zone:
Zone I = 190°C;
Zone II = 235°C;
Zone III = 280°C.

With these conditions 2,500 kg/h of polyethylene is produced with properties as shown in Table I.

Example 3

The process described here is similar to that of Example 2, with the difference that in Zone I instead of the lauroyl peroxide solution, 22 l/h of nonanoyl peroxide solution is introduced in a concentration of 37% by weight in mineral oil. 2,5000 kg/h of polyethylene is produced with properties as shown in Table I.

Example 4

The process described here is similar to that of Example 2, with the difference that in Zone II, instead of the terbutylperbenzoate solution, 14 l/h of nonanoyl peroxide solution is introduced in concentration of 37% in mineral oil.
The temperature of Zone II is 210°C.
With these conditions 2,600 kg/h of polyethylene is produced with properties as given in Table I.

Examples 1 to 4 illustrate polymerization without using terbutyl perneodecanoate initiator. The following Examples are examples of the method of the invention.

Example 5

Ethylene is compressed and supplied to an autoclave with a capacity of 250 l provided with a stirrer and divided into four reaction zones by baffles attached to the stirrer. The zones are fed with different reactants as follows:
Zone I - 5,000 kg/h of ethylene together with 27 l/h of terbutyl perneodecanoate solution in concentration of 25% by weight in isododecane.
Zone II - 9,000 kg/h of ethylene together with 14 l/h of nonanoyl peroxide solution in concentration of 37% by weight in mineral oil.
Zone III - 5,000 kg/h of ethylene together with 17 l/h of terbutyl peroctoate solution in concentration of 4% by weight in mineral oil.
Zone IV - 2.8 l/h of diterbutyl peroxide solution in concentration of 3% by weight in mineral oil.
Ethylene input temperature is 35°C.
Reaction pressure = 1400 atm.
Temperatures for each zone:
Zone I = 165°C
Zone II = 175°C
Zone III = 220°C
Zone IV = 280°C

With these conditions 3,400 kg/h of polyethylene is produced with properties as shown in Table I.

Example 6

The process described in this Example is similar to that of Example 2, with the difference that in Zone I, instead of the lauroyl peroxide solution, 35 l/h of terbutyl perneodecanoate solution is introduced in concentration of 15% by weight in isododecane.
The temperature of Zone I is 170°C.
With these conditions 2,600 kg/h of polyethylene is produced with characteristics as shown in Table I.

Example 7

The process described in this Example is similar to that of Example 2, with the difference

that in Zone I, instead of the lauroyl peroxide solution, 20 l/h of terbutyl perneodecanoate solution is introduced in concentration of 25% by weight in isododecane.
The temperature of Zone I is 160°C.
With these conditions 2.600 kg/h of polyethylene is produced with properties as shown in Table I.

TABLE I

PROPERTIES		EXAMPLES						
		1	2	3	4	5	6	7
M.F.I. g/ 10'	(a)	0.28	0.31	0.30	0.32	0.30	0.31	0.29
Density g/cc	(b)	0.9205	0.9208	0.9208	0.9210	0.9210	0.9215	0.9215
Swelling ratio	(c)	1.52	1.54	1.54	1.44	1.39	1.40	1.42
Gloss (u)	(d)	40	40	40	48	55	58	57
Haze %	(e)	20	22	22	18	16	14.7	16
Impact Strength F50.g	(f)	880	800	840	950	1000	1050	1000
Elongation at break %	(g)	500	525	500	675	725	725	700
Tensile Strength kgf/cm^2.min.	(h)	110	125	125	160	180	180	190

(a) ASTM D 1238 - 65 T
(b) BS 3412 : 1966
(c) Diameter ratio extruded/capillary
(d) ASTM D 2457 - 65 T
(e) ASTM D 1003-61
(f) BS 2782-306 F
(g) ASTM D 1248-68
(h) ASTM 638-67

WHAT WE CLAIM IS:-

1. A method for the polymerization of ethylene in one or more reaction zones at a pressure of over 400 atm. and a temperature of 100-300°C in the presence in at least one of the reaction zones of terbutyl perneodecanoate (as hereinbefore defined) which is introduced as a 5-40% by weight solution in isododecane.

2. A method according to claim 1, wherein the polymerization is carried out in an autoclave having two or more reaction zones, said terbutyl perneodecanoate solution being introduced to a first one of said zones only and the temperature of such first zone being less than the temperature of the or each other zone.

3. A method according to claim 1 substantially as hereinbefore described in any one of Examples 5 to 7.

4. Polyethylene when made by the method of any one of claims 1 to 3.

Agents for the Applicants,
SYDNEY E. M'CAW & CO.,
Chartered Patent Agents,
Saxone House,
52-56 Market Street,
Manchester M1 1PP.

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